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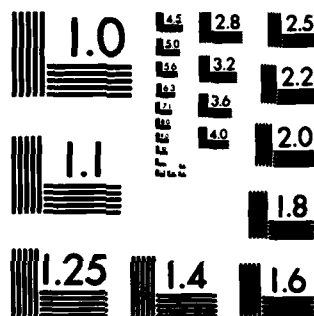
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Coumarin laser dyes upon excitation degrade to produce products which absorb at the lasing wavelength. This results in attenuation of dye laser output. Modes of degradation of coumarin dye lasers under both anaerobic and aerobic conditions were determined and methods of stabilization of dye lasers were established. Originator furnished keywords include: 85 01 29 144		

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CHEMICAL STABILIZATION OF LASER DYES

FINAL REPORT

TAD H. KOCH

NOVEMBER 1984

U.S. ARMY RESEARCH OFFICE

DAAG 29-81-K-0146

UNIVERSITY OF COLORADO

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Army Final Report

Problem Studied

Many laser dyes, especially the coumarins, are photolabile when employed in dye lasers. Products are formed which absorb at the lasing wavelength, and this absorption significantly attenuates the laser output. As model systems, the photodegradation of Coumarin 311, 7-dimethylamino-4-methylcoumarin, and Coumarin 1, 7-diethylamino-4-methylcoumarin, was studied under both aerobic and anaerobic conditions. A major goal was the development of stabilizing additives for dye lasers.

Summary of Important Results

a) Anaerobic conditions. Addition of the sulfur free radical chain transfer agents ethanethiol and ethyl disulfide retard the rate of formation of photoproducts absorbing at the lasing wavelength from irradiation of Coumarin 311. The stabilizing effect of the chain transfer agents was proposed from the results of deuterium labeling experiments. Deuterium incorporation in the coumarin from irradiation in the presence of ethanethiol and ethyl disulfide as a function of reaction conditions indicate that excitation of Coumarin 311 leads to free radicals. Free radicals result from bimolecular reaction of excited state coumarin with ground state coumarin. The chain transfer agents react with the coumarin free radicals to restore the coumarin. In the absence of these stabilizers, product formation is proposed to occur through radical combination reactions. The results of mechanistic studies are summarized in Scheme 1.

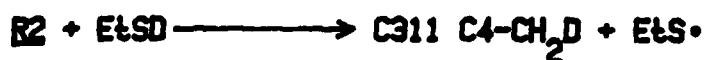
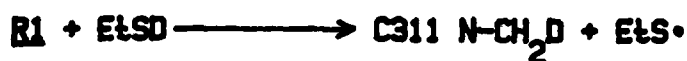
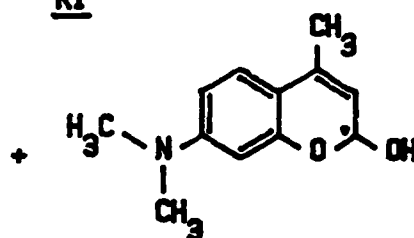
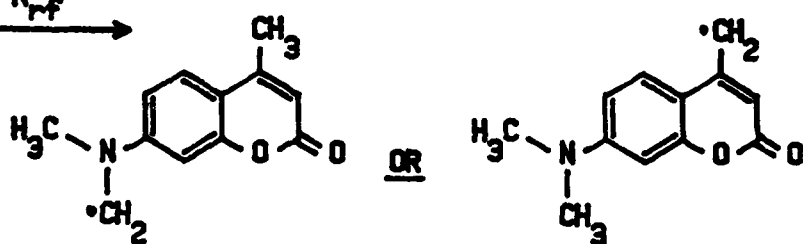
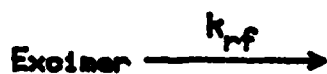
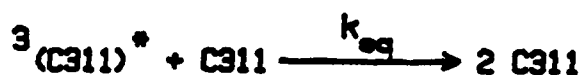
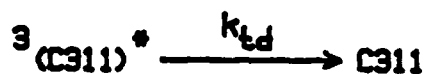
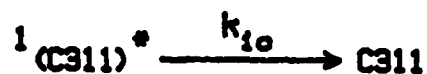
Ethanethiol and ethyl disulfide decrease the rate of power loss from a Coumarin 1 dye laser. The naturally occurring SH-containing amino acid cysteine acts similarly.

b) Aerobic conditions. The singlet oxygen quencher DABCO, 1,4-diazabicyclo[2.2.2]octane, was found to stabilize a variety of laser dyes, including the coumarin dyes, in several dye lasers. Extensive mechanistic studies of Coumarin 311 stabilization by DABCO were performed. The role of DABCO is complex and appears to involve more than singlet oxygen quenching. The major products formed which absorb at the lasing wavelength from aerobic irradiation of Coumarin 311 are 7-dimethylaminocoumarin-4-carboxaldehyde and 7-dimethylaminocoumarin-4-carboxylic acid. Other products isolated from the irradiation are 7-methylamino-4-methylcoumarin, 7-formylmethylamino-4-methylcoumarin, and 7-dimethylamino-4-hydroxymethylcoumarin. A proposed mechanism for product formation from radicals R1 and R2 is shown in Scheme 2. The formation of radicals R1 and R2 occurs in three ways: in a reaction of an excited coumarin with a ground state coumarin, in a reaction of singlet oxygen with ground state coumarin, and in a reaction of triplet oxygen with singlet excited coumarin. DABCO is proposed to inhibit the formation of products absorbing at the lasing wavelength by quenching singlet oxygen resulting from oxygen quenching of coumarin triplets and by forming a charge transfer complex with oxygen and this complex quenching coumarin triplets.

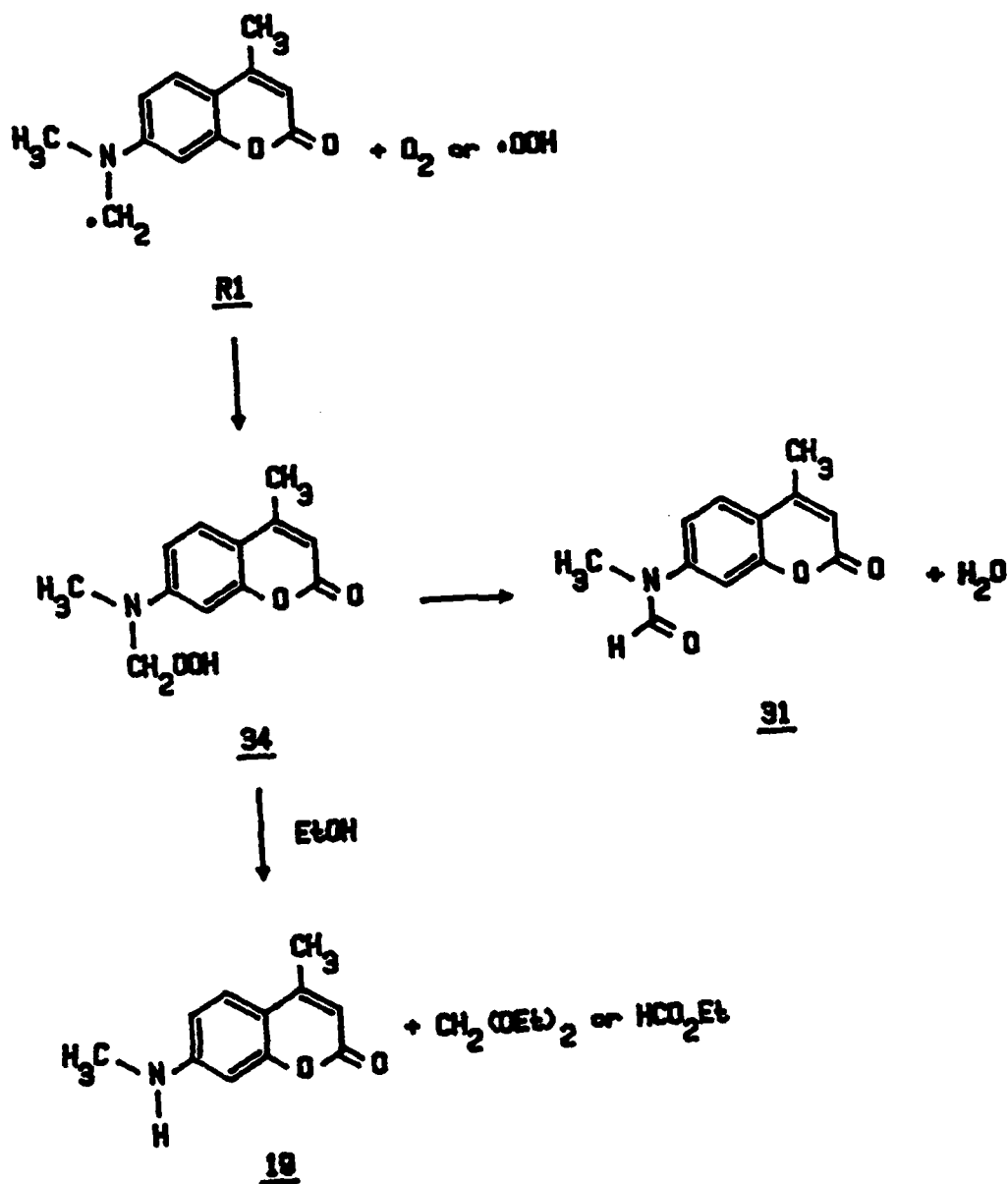
Dyes in dye lasers stabilized by DABCO include Coumarin 1, Coumarin 120, Coumarin 314, Rhodamine B, BBQ, and Stilbene 420. In general the stabilizing effect of DABCO appears to involve at least in part the quenching of singlet oxygen resulting from oxygen quenching of dye triplets.

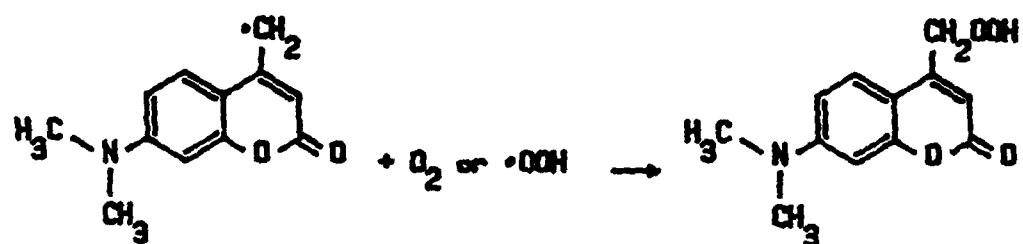
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Scheme 1



Scheme II

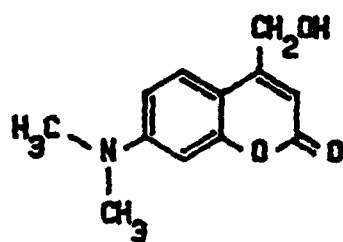




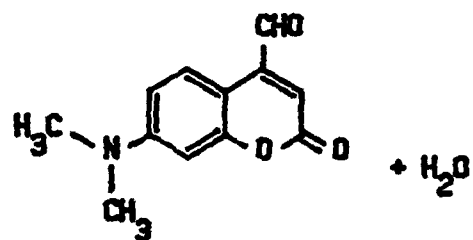
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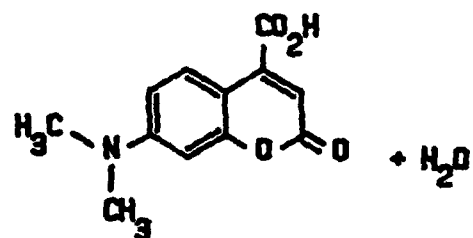
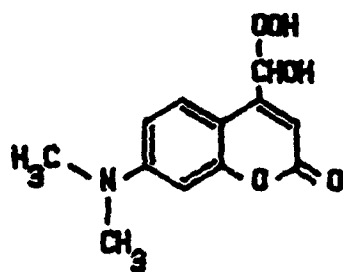
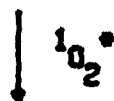
Cleavage and
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Robert von Trebra, graduate research assistant, Ph.D. (to be received 12/84).

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